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Survey of pesticide residues in pomes fruits and tomatoes from local and foreign productions

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Introduction

The protection of human health from exposure to pesticide residues in foodstuffs remains a major objective. Pesticides constitute a very important group of chemical compounds due to their widespread use in agricultural practice for field and post harvest protection. As they are often toxic, the survey of their residues in food is of very large interest. Indeed, over 1000 compounds may be applied to agricultural crops in order to control undesirable moulds, insects or weeds. To ensure the food safety for consumers, numerous legislations as the EU directives (1) or the Swiss regulations (2) as well as Codex alimentarius of FAO/WHO have established maximum residue limits (MRL) for pesticides in foodstuffs. For pesticide monitoring, gas chromatography (GC) with electron capture detection (ECD), nitrogen-phosphorus detection (NPD) and mass spectrometry (MS) detection are the most widely used techniques since many years (3). Recently, some applications using GC-MS/MS for pesticide determination in fruits and vegetables have been described in the literature (4, 5). However, many of them, which are thermally unstable or non-volatile such as carbamates, benzimidazoles or triazoles, are difficult or impossible to analyze using these techniques. Liquid chromatography (LC) coupled with tandem mass spectrometry (MS/MS) offers a powerful tool for the determination of these compounds in food samples (6–8). A LC-MS/MS method with a simplified extraction procedure was developed as a complement to traditional GC pesticide determination in order to carry out an effective control of pesticide residues in fruits and vegetables (9).

This paper presents the overall procedure for pesticide residues analysis and its application for the survey of pome (apples and pears) and tomatoes of local production in comparison with imported products. Around 150 apples and pears were sampled directly from Geneva area farmers from September to October 2002. For tomatoes, there are about 85 samples of the Geneva production, which were taken and analyzed between May and September 2003. In parallel, imported samples of apples, pears and tomatoes were also analyzed and the results compared with local production.

Experimental

Sampling

Pome

Samples were taken directly from Geneva area farmers, in local cooperatives and on the market in Geneva area: 131 apples and 31 pears from almost all local farmers were taken during September–October 2002. In addition, imported products were sampled directly on the Geneva market during two years (2002–2003). This represents 35 apples and 36 pear samples from Argentina, Belgium, Chile, France, Italia, New-Zealand, Portugal, South Africa, Spain and Turkey.

Tomatoes

Geneva has 26 tomato farmers located in its territory or in French free zone border. With a volume of around 4500 tons per year, this corresponds nearly to 20 % of the Swiss tomato production. This production is commercialized on the Swiss market; 30 % in the Geneva area. In order to perform a survey of pesticides residues in tomatoes of local production, we collaborated with the "Union Maraîchère de Genève (UMG)" which is the major cooperative for fruits and vegetables from local farmers. The UMG has accepted to control its overall production before commercialisation on the Swiss market and collected samples directly at the farmer. Between May and September 66 lots of tomatoes provided by the UMG with the indication of the pesticide treatments done for each sample were analysed. Simultaneously, since the beginning of 2003, Swiss and imported tomatoes were collected from the Geneva market or directly from importer. Finally, 169 tomato samples were analyzed for pesticides residues 85 Swiss samples (mainly from Geneva) and 84 samples originating from Spain, Netherlands and Morocco. Among these 169 samples, 14 samples originated from certified organic agriculture.

Analytical Methods

In order to screen a very large number of pesticides, we used two different multiresidue methods. The overall schematic procedure is shown in figure 1.

Apolar pesticides such as organochlorine and organophosphorous fungicides and insecticides are extracted with acetonitrile. After addition of water, pesticides are extracted by liquid-liquid extraction with hexane. The hexane portion is collected and analyzed by gas chromatography (GC) on analytical capillary columns of different polarities (DB-5 and SPB-20) with electron capture (ECD) and nitrogen-phos-

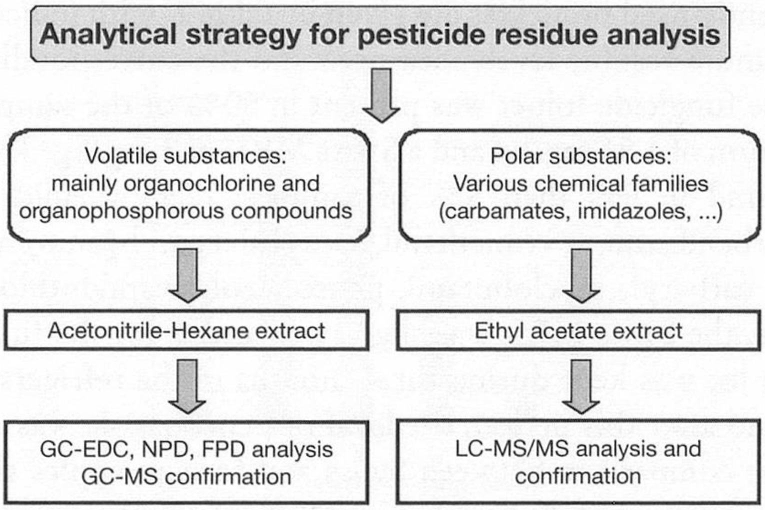

Figure 1 **Overall scheme of the analytical strategy for the pesticide residues survey**

phorus (NPD) detection. In case of ambiguous identification or for not compliant samples, confirmations are carried out with mass spectrometry (MS) detection.

Polar pesticides such as carbamates, benzimidazoles or triazoles, are extracted from samples with ethyl acetate. Except for a concentration step, no additional clean-up is necessary. Analyses are performed by liquid chromatography coupled to electrospray ionization and tandem mass spectrometry (LC-ESI-MS/MS) (9). This multiresidue method allows the determination of 74 pesticides commonly used in crop protection.

Results and discussion

Pome

In table 1 the results obtained for apples and pears of Swiss and foreign origin are summarised. Results showed that 75 % of samples contained pesticide residues. However, for almost all samples, the pesticides concentrations were far below the MRL's. This demonstrates that treatments were done correctly and that dose, number of applications and withdrawal times before harvest were respected.

Table 1
Results of the survey of pesticide residues in Swiss and foreign apples and pears

Fruits	*Origin*	*Number of samples*	*Samples without residues*	*Samples with residues below MRL*	*Samples with residues above MRL*
Apples	Swiss	131	26 (20 %)	104 (79 %)	1 (1 %)
	Foreign	35	16 (46 %)	19 (54 %)	–
Pears	Swiss	31	16 (52 %)	15 (48 %)	–
	Foreign	36	10 (29 %)	25 (69 %)	1 (2 %)
	Total	233	68 (29 %)	163 (70 %)	2 (1 %)

For apples, 20 active substances used as fungicides or insecticides were detected. The most frequently used pesticides are given in Table 2, with indication of the minimum and maximum residue levels measured and the corresponding Swiss MRLs. For example, the fungicide folpet was present in 50 % of the samples with a maximum concentration of 1.51 mg/kg and a Swiss MRL of 3 mg/kg. The following pesticides were found in less than 5 % of samples: dichlofluanid, diphenylamine, acetamiprid, carbendazim, pyrimethanil, hexythiazox, bromopropylate, difenoconazol, sulfur, carbaryl, myclobutanil, penconazole, vamidothion, thiabendazol. In only one case, the Swiss MRL was slightly exceeded for the fungicide penconazole. This apple lot was kept during three months in the refrigerator before commercialisation and after this period, the level of penconazole was compliant to the Swiss MRL. The comparison between Swiss and foreign apples showed only few differences, except the use of diphenylamine (35 % of positive sample of foreign origin) for post-harvest treatment to ensure the fruit's quality during transportation. As shown in Figure 2, numerous samples contained more than one pesticide residue. Sometimes, six different active substances were observed in the same sample. In addition, analysis method improvements, as the very high sensitivity and selectivity of the LC-MS/MS, allowed showing up residues, which were not detected few years ago. For pears, approximately the same substances as for apples were found: captan, cyprodinil, fenitrothion, fenoxycarb, fenpropathrin, fludioxonil, flusilazole, folpet, indoxacarb, procymidone and trifloxystrobin. One MRL exceedance was observed for flusilazole in a foreign product. As shown in Figure 2, the number of residues per sample in pears was also lower than for apples.

Table 2
Frequeently found substances in pome, median, maximum and minimum levels and corresponding Swiss MRL

Pesticide	*% of positive samples*	*Levels min-max [mg/kg]*	*Median [mg/kg]*	*Swiss MRL [mg/kg]*
Folpet	49 %	0.02–1.51	0.11	3
Pirimicarb	30 %	0.01–0.10	0.02	1
Trifloxystrobin	27 %	0.02–0.22	0.03	0.5
Indoxacarb	15 %	0.01–0.05	0.02	0.5
Fenoxycarb	11 %	0.01–0.06	0.01	0.3
Captan	7 %	0.01–0.61	0.06	3

According to the results of this survey, even if pesticide residues were present in a majority of samples, the level was generally low and the quality of pome sold in Geneva area was very satisfying. Almost all samples were compliant with the Swiss regulations (2).

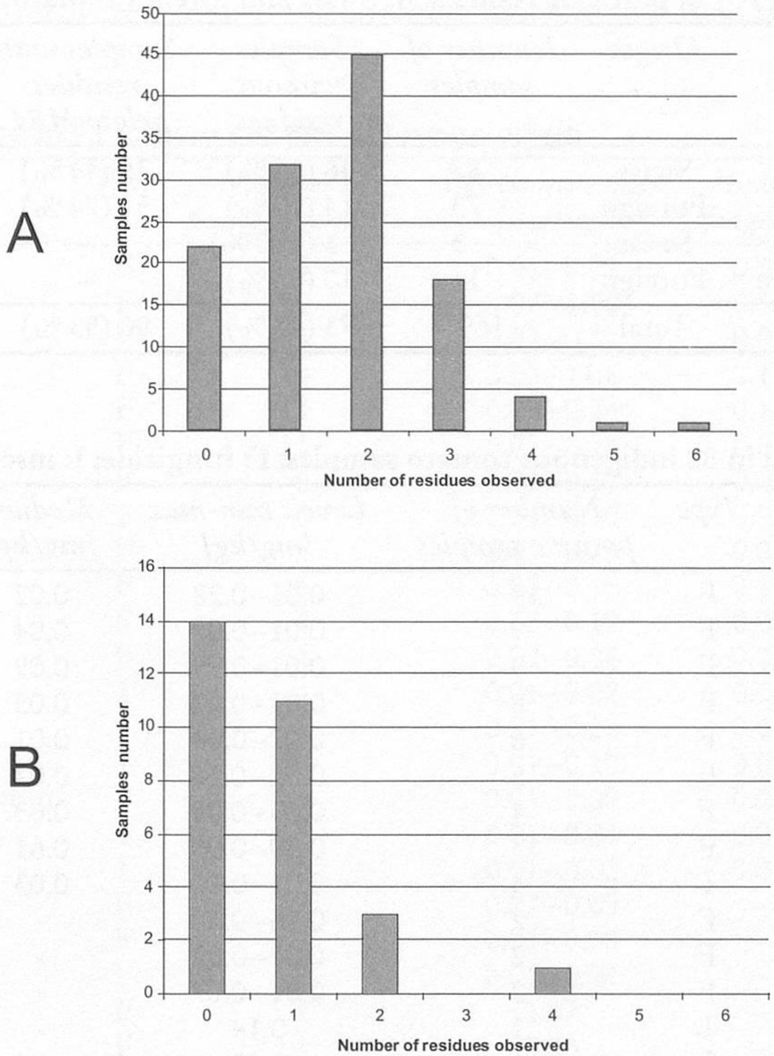

Figure 2 **Number of pesticide residues found per sample. A) Apples; B) Pears**

Tomatoes

Table 3 summarises the results obtained from the tomato survey. Unlike the results of pome, a significant difference has been observed between local and imported products. More than 50% of indigenous tomatoes were free from pesticide residues and no MRL exceedance was recorded. The pesticides found in the 36 positive indigenous samples were mainly fungicides and more rarely insecticides. This can be explained by the intention of the local farmers to use as far as possible biological predators (as for example *Macrolophus caliginosus)* as auxiliaries rather than chemical products against pests. Table 4 shows the list of pesticides found in indigenous products, with indication of the maximum concentration found and the corresponding Swiss MRL's. The mixture of cyprodinil and fludioxonil (Switch®), carbendazim and chlorothalonil were the most used pesticides against mould. However, it must be noted that 2003 was a year particularly favourable for the local farmers due to a very dry summer, which had greatly limited the hazards of mould development.

Table 3
Results of the survey of pesticide residues in Swiss and foreign tomatoes

Production	*Origin*	*Number of samples*	*Samples without residues*	*Samples with residues below MRL*	*Samples with residues above MRL*
Tomatoes	Swiss	82	46 (56 %)	36 (44 %)	–
	Foreign	73	14 (19 %)	54 (74 %)	5 (7 %)
Tomatoes from	Swiss	3	3 (100 %)	–	–
organic agriculture	Foreign	11	10 (90 %)	–	1 (10 %)
	Total	169	73 (43 %)	90 (53 %)	6 (4 %)

Table 4
Substances found in 82 indigenous tomato samples: F: fungicide; I: insecticide

Pesticides	*Type*	*Number of positive samples*	*Levels min-max [mg/kg]*	*Median [mg/kg]*	*Swiss MRL [mg/kg]*
Cyprodinil	F	14	0.01–0.28	0.02	0.5
Carbendazim	F	9	0.01–0.07	0.04	0.5
Chlorothalonil	F	9	0.01–0.99	0.09	2
Fludioxonil	F	8	0.03–0.20	0.05	0.5
Diethofencarb	F	6	0.01–0.04	0.01	0.5
Dimethomorph	F	5	0.02–0.18	0.07	0.2
Propamocarb	F	4	0.03–0.09	0.03	0.2
Fenhexamid	F	3	0.60–0.90	0.61	1
Pymetrozine	I	3	0.01–0.10	0.03	0.5
Folpet	F	2	0.16–0.30	-	3
Myclobutanil	F	2	0.01–0.02	-	0.1
Triforine	F	2	0.04–0.07	-	0.1
Buprofezine	I	1	0.14	-	0.3
Pirimicarb	I	1	0.05	-	1
Pyrimethanil	F	1	0.01	-	2

F: fungicide; I: insecticide

80 % of the imported samples contained pesticide residues and MRL exceedance was observed for 5 samples. In 2 cases, several substances with concentration above the MRL were found. As shown in Table 5, imported tomatoes were more contaminated by pesticide residues than indigenous samples. Effectively, 32 different pesticides were detected with about 1/3 of insecticides and 2/3 of fungicides. These results can be explained by the diversity of the samples origin (Italy 30 samples, Spain 16, Tunisia 11, Morocco 6, Netherlands 4, France 3, various 3) and therefore the various practices and legislations concerning plant health treatments of each country.

Approximately the same substances as in Switzerland were detected beside the very often used procymidone, iprodione and azoxystrobin. It must also be noted that some pesticides found (indicated in Table 5 with an asterisk) are not approved by the Swiss legislation and therefore not allowed in Switzerland for tomatoes. In these cases, the MRL indicated in Table 5 corresponds to the recommendations given by the Swiss federal office of public health. Concerning samples with MRL exceedance, the measured concentrations were much higher than the MRL.

Table 5
Substances found in 73 tomato samples of foreign origin

Pesticide	*Type*	*Number of positive samples*	*Levels min-max [mg/kg]*	*Median [mg/kg]*	*Swiss MRL [mg/kg]*
Carbendazim	F	21	0.01–0.07	0.02	0.5
Procymidone	F	20	0.07–1.80	0.38	2
Cyprodinil	F	15	0.01–0.25	0.04	0.5
Chlorothalonil	F	14	0.03–11.6	0.15	2
Iprodione	F	11	0.03–0.24	0.15	5
Azoxystrobin	F	11	0.01–0.18	0.02	2
Pyrimethanil	F	6	0.01–0.12	0.02	2
Fludioxonil	F	6	0.01–0.10	0.03	0.5
Oxadixyl	F	5	0.01–0.25	0.08	0.10
Dichlofluanid	F	5	0.05–0.15	0.11	5
Metalaxyl	F	4	0.03–0.10	0.05	0.05
Difenoconazole	F	4	0.02–0.06	0.03	0.5
Acetamiprid *	I	4	0.01–0.02	0.02	0.2
Buprofezine	I	3	0.01–0.20	0.02	0.3
Endosulfan	I	3	0.01–0.10	0.08	0.5
Thiophanate methyl	F	3	0.01–0.09	0.04	0.5
Carbofuran	I	3	0.01–0.05	0.03	0.1
Pyridaben *	I	3	0.01–0.03	0.01	0.1
Cymoxanil	F	2	0.02–0.09	–	0.05
Diethofencarb	F	2	0.01–0.08	–	0.5
Tebuconazol *	F	2	0.02–0.04	–	0.2
Mepronil *	F	1	1.07	–	0.05
Captan	F	1	0.33	–	3
Chlorpyrifos	I	1	0.25	–	0.5
Thiabendazol	F	1	0.09	–	0.05
Imazalil	F	1	0.06	–	0.5
Malathion	I	1	0.06	–	3
Penconazol	F	1	0.05	–	0.2
Methiocarb	I	1	0.04	–	0.05
Myclobutanil	F	1	0.03	–	0.1
Imidacloprid *	I	1	0.03	–	0.3
Indoxacarb *	I	1	0.02	–	0.2

F: fungicide; I: inseticide; * Substance not allowed in tomato cultivation in Switzerland.

This survey included also some samples issued from certified organic culture. The great majority of these samples were imported, mainly from Italy. Only one sample was detected with pesticides residues and consequently was not in accordance with the Swiss law concerning organic agriculture (10). However, the concentration levels measured were very low: 0.01 mg/kg cyprodinil and 0.01 mg/kg pyrimethanil. For such low concentration levels, pesticide residues derive probably from a contamination occurring from a pesticide treatment of a neighbouring field or during the handling or conditioning of the tomatoes but not from an intentional plant protection treatment.

Conclusion

The analytical methodology presented in this work for the survey of pesticide residue in crops is efficient and allows the detection of a very large number of plant health treatments. Pesticide residues in pome and tomatoes were under the MRL for indigenous production. These results demonstrate that crop treatments were done correctly and that dose, number of applications and withdrawal times before harvest were respected. Few differences were observed between local and foreign pome production except the use of the fungicide diphenylamine. For tomatoes, the foreign production was contaminated with higher levels of pesticides and more insecticides were found. Furthermore, several MRL exceedances, sometimes with high levels, were observed.

Summary

Pesticide residue analysis in food remains a continuous problem. This survey becomes increasingly difficult due to the fact that many active substances are used today in modern agriculture. In order to obtain an efficient screening, our laboratory has developed an analytical strategy with the complementary analysis of apolar pesticides by GC with ECD, NPD and MS detection and polar pesticides with LC-MS/MS. This methodology was applied to the survey of pome and tomatoes, which are the most important fruit production in the Geneva area. The results from samples directly collected from farmers were compared with imported samples. For local products, the situation was very satisfying for both crops. Pome health treatments were numerous, but were correctly carried out. The imported tomatoes showed a higher contamination with pesticides and several non compliant samples.

Résumé

L'analyse de résidus de pesticides dans les denrées alimentaires reste un problème d'actualité. Cette recherche de résidus est de plus en plus difficile car de très nombreuses matières actives sont utilisées aujourd'hui dans l'agriculture moderne. Afin de pouvoir couvrir le plus large spectre possible, notre laboratoire a développé une stratégie analytique comprenant l'analyse complémentaire des pesticides apolaires par chromatographie gazeuse avec détection ECD, NPD et MS, et des pesticides polaires par LC-MS/MS. Ces analyses ont été appliquées à deux programmes de contrôle concernant les fruits à pépins (pommes et poires) et les tomates. En effet, ces deux productions sont importantes pour la région genevoise et il était intéressant de faire une étude quant aux résidus de pesticides contenus dans ces cultures locales. Les résultats issus d'échantillons prélevés directement chez les producteurs ont été comparés à ceux d'échantillons d'origine étrangère. Globalement, la situation genevoise est très bonne pour les deux types de cultures. Les traitements phytosanitaires des fruits à pépins sont nombreux, mais correctement effectués puisqu'un seul léger dépassement des normes en

vigueur a été constaté. Pour les tomates, la situation locale est encore meilleure, surtout comparée aux productions étrangères.

Zusammenfassung

Die Pestizidanalytik von Lebensmitteln bleibt ein aktuelles Problem. Die Rückstanduntersuchungen werden immer anspruchsvoller, da heute in der Landwirtschaft eine grosse Zahl von Wirkstoffen eingesetzt wird. Um ein möglichst breites Analysenspektrum abzudecken, hat unser Labor eine analytische Strategie entwickelt, welche nebst der Prüfung auf apolare Pestizide mit Gaschromatographie mit ECD-, NPD- und MS-Detektion, die Analyse von polaren Pestiziden mit LC/MS/MS umfasst. Diese Analysenstrategie wurde in Rahmen von zwei Kontrollprogrammen erprobt. Kernobst (Äpfel und Birnen) und Tomaten sind wichtige Landwirtschaftsprodukte der Genfer Region. Es war deshalb von besonderem Interesse, die Rückstandssituation bei diesen Produkten genauer zu untersuchen. Die direkt bei den inländischen Erzeugern erhobenen Stichproben wurden mit ausländischer Ware verglichen. Insgesamt waren Kernobst und Tomaten aus der Schweiz bezüglich Rückstände als gut zu bezeichnen. Das Kernobst wurde mit zahlreichen Wirkstoffen behandelt. Jedoch erfolgte die Anwendung der Spritzmittel vorschriftsgemäss und führte deshalb selten zu Toleranzwertüberschreitungen. Inländische Tomaten waren noch weniger mit Rückständen belastet als das Kernobst, besonders im Vergleich zur ausländischen Ware.

Key words

LC-ESI-MS/MS, tandem mass spectrometry, pesticides residues, food analysis

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